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ABSORPTION AND RETENTION OF HYDROCYANIC ACID BY FUMIGATED FOOD PRODUCTS. PART II[1]

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INTRODUCTION

The work reported in 1923 in Department Bulletin No. 1149 of the United States Department of Agriculture showed that different foodstuffs absorb and retain varying quantities of hydrocyanic acid. The cases of agreement among closely related products are not so marked that the absorption by one foodstuff may be confidently predicted from that of another. This investigation was therefore extended to other fumigated foodstuffs, and the removal of hydrocyanic acid from foodstuffs by boiling, as in cooking, was studied. The results thus obtained, together with references to the work and opinions of other investigators, are given in the following pages.

REVIEW OF LITERATURE

Lutrario (*6*)[2] exposed foodstuffs for 80 minutes in an experimental chamber, to a gas obtained from 5 grams of 88 per cent commercial sodium cyanide for each cubic meter of space (at the rate of about half an ounce for each 100 cubic feet). Table 1 is compiled from his results.

In these experiments the dosage of hydrocyanic acid gas was smaller and the time of exposure was shorter than is usual in fumigating warehouses or factories.

Heerdt (*4*) stated that foods with a high moisture content take up notable quantities of hydrocyanic acid on fumigation. If the fumigant

[1] Part I was published as Department Bulletin 1149, May 9, 1923.
[2] Italic numbers in parenthesis refer to Literature Cited, p. 8.

retained exceeds 12 milligrams in 100 grams of the substance (120 parts per million) these foods are injurious. He concluded that uncovered fluids and moist foods, especially oils and fats, should not be exposed to hydrocyanic acid gas.

TABLE 1.—*Hydrocyanic acid in fumigated foodstuffs (Lutrario)*

Product and condition for fumigation	Hydrocyanic acid found (parts per million)		
	Immediately	After 1 hour	After 24 hours
Fresh beef:			
Ground	99.5		[1] 9.7
In pieces (10 cm. cubes)	60.5	45.1	11.8
Bread:			
Slices	44.3	27.0	4.3
Whole loaves (500 grams)	34.6	17.0	1.0
Tea:			
In closed paper packet	38.0	35.0	10.0
Open	59.0	48.0	16.8
Wine:			
At the surface	22.7		9.2
At a depth of 17 cm	15.4		8.2
Lard (slices 4 cm. thick)	19.8	[1] 7.6	
Cow's milk:			
At the surface	13.5	2.4	[1] 1.0
At a depth of 18 cm	2.2		
Olive oil:			
At the surface	4.9	1.6	.0
At a depth of 10 cm	1.1		
Apples (fresh, whole)	15.1		4.3
Figs (dry)	8.6	6.5	3.7
Peaches (fresh, whole)	16.2		4.5
Raisins (dry)	10.8	7.6	4.8
Beans (dry)	5.4	5.1	4.3
Potatoes (whole)	.5	.0	
Wheat (in a sack)	10.8	9.2	2.2
Wheat flour (in a sack):			
At the surface	23.7	18.9	3.2
At a depth of 35 cm	5.4	3.8	
Honey (at the surface)	3.2		.9
Fruit marmalade (at the surface)	4.9		1.2

[1] Fumigated bread, meat, milk, and lard were fed to dogs, in approximately 500-gram portions, one or two hours after exposure, without injury.

DeOng and Roadhouse (*3*) exposed cheese for 24 hours to a gas made by using 3 to 10 ounces of sodium cyanide per 1,000 cubic feet. Paraffined, unparaffined, and cut samples of cheese of varying age, made from whole milk, half-skim, and skim milk, absorbed no gas, or only negligible quantities that were dissipated by aeration for a few hours. Expert cheesemakers, chemists, and others detected no abnormal flavors in the fumigated cheese, nor did this cheese have any harmful effects on mice.

Simmons (*7*) reported that Camembert, Cheddar, and Swiss cheese fumigated with hydrocyanic acid, in quantities sufficient to kill the cheese skipper (*Piophila casei L.*), retained some of the fumigant for at least 24 hours. Cheddar cheese did not absorb as much of the fumigant as Camembert and Swiss cheese, which retained a good deal. Simmons suggested that, until extensive quantitative analyses are made of each variety of cheese, fumigated with different dosages for varying periods, followed by airing for varying periods, cyanide fumigation of cheese should not be recommended.

Bonjean (*2*) reported the fumigation of foodstuffs in the cabin and hold of a vessel. In the cabin about three-fourths of an ounce of sodium cyanide per 100 cubic feet of space was used with an exposure of five hours. In the hold the dosage was one-third of an ounce of sodium cyanide per 100 cubic feet and the exposure was one hour, followed

by aeration from the open hatches for four hours. Hydrocyanic acid was found in almost all of the fumigated foodstuffs, the quantity increasing with the water content, in the following order: Water; banana peel; banana fruit; oranges; edible oil; shell eggs; egg albumen; bread; tea; flour; wheat, oats, and peanuts; beans and corn. The last two groups contained very little fumigant. Apparently Bonjean did not determine the exact quantity of hydrocyanic acid retained. Hydrocyanic acid, he stated, was not held in foods in quantities sufficient to be toxic.

Among the advantages of using hydrocyanic acid gas enumerated in a preliminary report of the board appointed by the Surgeon General of the United States Public Health Service to investigate the fumigation of ships (*1*) it is stated that this gas does not affect foodstuffs.

Stock and Monier-Williams (*8*) made the following statement:

> Experiments carried out during an experimental fumigation at Tilbury Docks showed that foodstuffs of the most varied kind, meat, butter, flour, &c., did not absorb more than traces of hydrogen cyanide under the conditions of the experiment. It would seem probable that even if the gas were absorbed in small amounts, it would be rapidly evolved or oxidised on subsequent exposure to air or on cooking. Nevertheless it has been the practice to remove moist or liquid foodstuffs such as meat, milk, &c., before fumigation, and either to empty or to seal up fresh-water tanks.

The literature contains references also to the use of a mixture which is said to contain about 90 per cent of cyanocarbonic ester and 10 per cent of chlorocarbonic ester. The cyanocarbonic ester is said to break down immediately in contact with moisture, to form hydrocyanic acid. (The chlorocarbonic ester is used as an indicator on account of its lacrymatory power.) Fumigation with this product thus corresponds to some extent to fumigation with hydrocyanic acid. Jansen, Schut, and Wagenaar (*5*) fumigated food products in a ship with this mixture and then calculated the quantity of hydrocyanic acid absorbed to the original material. Their results are of the same order as those found when hydrocyanic acid is used as the fumigant, making allowance for the fact that their fumigant contained only about 24 per cent of cyanogen.

EXPERIMENTAL WORK

DRIED FRUITS

Dried fruit does not cost as much to ship and is not as subject to decay as fresh fruit. It is, however, subject to attack by insects. The problem of insect control becomes particularly serious when it is necessary to carry dried fruit over from one year to another. Because of the high cost of the present practice of keeping dried fruit in cold storage, Dr. L. C. Corbett of the Bureau of Plant Industry pointed out the value to the industry of fumigation with hydrocyanic acid to prevent insect injury, if it could be done without injuring the fruit for consumption. Experiments were therefore undertaken to find how much gas these products would retain after fumigation and how long they would hold it.

Dried fruits were bought in the open market. In most cases commercial packages were fumigated without being opened until the fumigation was finished. In all cases, small quantities were fumigated without any protection from the gas.

The fumigations were carried out at atmospheric pressure by the "pot" method, using sodium cyanide, sulphuric acid, and water, in the

TABLE 2.—*Hydrocyanic acid in fumigated dried fruits*

Product and condition for fumigation	Temperature of fumigation		Hydrocyanic acid present (parts per million)							
				Stored at about 70° F. for—				Stored at about 40° F. for—			
	Beginning	End	Initial	1 day	7 days	30 days	90 days	1 day	7 days	30 days	90 days
	° F.	° F.									
Apples, dried	81	74									
Spread on paper			33	11	9	7	4				
In 3-pound cloth sack			44						55	22	11
In original box (about 25 pounds)—											
Top			11	4	4	3	2	4	4	4	3
Center			10								
Apricots, dried	81	74									
In 3-pound cloth sack			24	22	15	11	5		26	18	9
In original 25-pound box—											
Top and center			0								
Dates	85	78									
Fumigated loose			44	17	11	2	3		39	11	
In unopened 12-pound box—											
Top			9	6	9	3					
Center			9		4	0					
Figs	80	76									
Washed—											
In open paper sack			88	22	17	7	4	22	28	22	11
Pulled—											
In unopened 5-pound box—											
Top			39	11	4	2	0		7	7	2
Center			8	4							
In open sack			22	31	9	11	4		18	18	9
In unopened 20-pound box—											
Top			9	6	0	0			0		
Center			0	0	0	0					
Peaches, dried, in 3-pound cloth sack	80	75	27	27	20	5	0	27	28	11	7
Pears, dried, fumigated loose	70	66	39	11	6	4	3		9	9	3
Prunes	80	75									
In original 25-pound box—											
Outer layer			7	4	3	2	0	4	4	4	0
Center			7								
Stones			0								
In 3-pound cloth sack			31	24	11	7	2	24	27	11	4
Stones			0								
Raisins	90	83									
Seedless—											
In unopened carton			11	13				13	13	18	5
Flaps turned back			28	22	16	7	2				
Poured out on paper			26	18	16	10	3				
Seeded Muscat—											
In unopened carton			2	3			2	3	3		
Top flaps open			2	1	2	3	0				
Carton and wrapper removed			31	11	11	4	0				
Cluster, exposed in open			18	15			0	15	16	13	
Raspberries, black	85	78									
Fumigated in 3-pound cloth sack			181	99	44	22	22				
Fumigated loose			132	99	44	28	22		132	44	44

proportions of 1 : 1½ : 2; that is, for every avoirdupois ounce of sodium cyanide 1½ fluid ounces of sulphuric acid and 2 ounces of water are used. The dosage was one ounce of sodium cyanide for each 100 cubic feet of space and the time of exposure, was about 18 hours. The temperature was noted at the beginning and at the end of the fumigation.

At the end of the fumigation period the products were removed from the fumigating chamber, and the hydrocyanic acid which they contained was determined by the method outlined in Department Bulletin, 1149, page 5. The first determination was made on the same day that the samples were removed from the chamber, but at least

an hour after the fumigation was completed. Most of the samples were then divided, one part being held at room temperature (about 70° F.) and the other in cold storage (about 40° F.). Hydrocyanic acid determinations were made on them at the end of 1, 7, 30, and 90 days. The results of these tests are shown in Table 2.

All of the dried fruits left unwrapped during fumigation absorbed hydrocyanic acid. Because of the wrappings, those fumigated in packages absorbed less—sometimes none. The box of dried apples was loosely packed and was lined with ordinary newsprint paper which permitted the gas to pass into the dried apples; in fact, it penetrated so well that the concentration in the center of the box was nearly as high as that in the outside layers. On the other hand, the box of apricots was tightly packed and was enclosed in waxed paper. No hydrocyanic acid was present in the packed apricots. The pasteboard carton of raisins gave little protection from the fumigant. The waxed paper tightly wrapped around the seeded raisins, however, was a very good protection. The figs in the 20-pound box were tightly packed. While a little hydrocyanic acid penetrated through the outer wrapping into the outer layer of fruit, none was found in the center of the box. Of course, such fumigation will not kill insects inside the box; in fact, live worms were found in the center of the box of figs.

Most of the fruits contained some hydrocyanic acid at the end of three months. They lost it more quickly when kept at room temperature than when kept in cold storage. The high original absorption by the black raspberries and the tenacity with which they retained the hydrocyanic acid are worthy of note. No explanation of this action is offered. Fumigation caused no physical deterioration or impairment of keeping qualities in the fruit.

Careful tests showed that no hydrocyanic acid was present in any of the fruit before fumigation.

TABLE 3.—*Hydrocyanic acid in fumigated candies, nut meats, chocolate, and cocoa*

Product and condition for fumigation	Temperature of fumigation		Hydrocyanic acid present (parts per million)							
				Stored at about 70° F. for—				Stored at about 40° F. for—		
	Beginning	End	Initial	1 day	7 days	30 days	90 days	1 day	7 days	30 days	90 days
	°F.	°F.									
Candy	79	72									
Chocolate creams, fumigated loose			11	7	3	0					
Coated nut meats, fumigated loose			22	9							
Chocolate creams in 1-pound box			11	9	3	1					
Coated nut meats in 1-pound box			18								
Pecans, meats, fumigated loose	70	66	180	11	3	1	0		11	7	3
English walnuts, meats, fumigated loose	70	66	200	11	5	4	2		9	8	3
Cocoa and chocolate	82	76									
Unopened, half-pound can of cocoa			0								
Half-pound can of cocoa, lid of can removed			192	110	44	31					
Unopened, half-pound package of chocolate			0								
Half-pound package of chocolate, fumigated open			15	11	7	4					

CANDY AND CANDY MAKING MATERIALS

Candy factories sometimes become infested with insects which might easily be destroyed by fumigation with hydrocyanic acid if it would not injure the candies and the materials from which they are made. Nut meats, candies, chocolate, and cocoa were fumigated and tested in the same way as the dried fruits (p. 3). The results of these experiments are given in Table 3.

The nut meats absorbed a very large proportion of hydrocyanic acid. Most of it was loosely held, however, so that one day after the fumigation the content had fallen to 11 parts per million. This residue was more firmly held and part of it remained for 30 to 90 days.

The difference in absorption between the chocolate creams and the coated nut meats seems to have resulted largely from the difference in surface. The coated nut meats were much rougher and therefore had a larger proportionate surface area.

The cocoa had a large original absorption and retained what it absorbed. The chocolate absorbed much less. This can be explained on the ground that the cocoa was finely powdered, giving each unit of weight a large surface area. Each unit of weight of the chocolate had a much smaller area of surface.

TABLE 4.—*Hydrocyanic acid in fumigated cereals, meat, cheese, and dried milk*

Product and condition for fumigation	Temperature of fumigation		Hydrocyanic acid present (parts per million)							
				Stored at about 70° F. for—				Stored at about 40° F. for—			
	Beginning	End	Initial	1 day	7 days	30 days	90 days	1 day	7 days	30 days	90 days
	°F.	°F.									
Cereals	74	66									
Prepared cereal in unopened package			10	2	0						
Prepared cereal, wax paper removed			11	6	4	0					
Wheat cereal in unopened carton			88	28	11	4					
Corn flakes in unopened carton			36	22	9	4					
Oat flakes in unopened carton			34	11	7	0					
Meats	82	85									
Bacon, in paper			100	28				28	7	3	
Bacon, sliced, in box			86	28	7	2					
Dried beef, in open			80	13	0						
Ham, sliced			170								
Hamburger steak, in open			66								
Hamburger steak, in paper			180								
Sausage, in open			190	39				39	26		
Sausage, in paper			220					55	13		
Cheese	63	60									
American Swiss, whole—											
Inedible portion (rind)			44								
Edible portion			0	0							
Imported Swiss, in 1-ounce piece—											
Wrapped in tin foil			0								
Unwrapped			149								
Roquefort, half-pound, unwrapped			110	49	14						
Cream—											
Wrapped in tin foil			110								
Unwrapped			110	55							
American, 1 pound, open			110	55	22						
Dried milk in open can	82	80	88	22	18	9					

CEREALS, MEAT, CHEESE, AND DRIED MILK

Cereals, meats, cheese, and dried milk are sometimes stored in factories which may become infested with insects. These products were fumigated and tested (p. 3). The results are given in Table 4.

The cereals absorbed hydrocyanic acid in quantities which could not be directly correlated with their properties or with the packages in which they were packed. The ordinary loose pasteboard boxes did little to keep the fumigant from the material in them. At the end of a week most of the hydrocyanic acid had disappeared.

All of the meat took up comparatively large quantities of hydrocyanic acid. Most of it had disappeared from the cured meat at the end of a week. The sausage held in cold storage did not lose the hydrocyanic acid as quickly as the cured meat.

When the surface of cheese was exposed directly to the fumigant the absorption was high. The hard rind of an American Swiss cheese was enough, however, to prevent the gas from penetrating. None was found even close under the rind, although some was present in the rind.

Tin foil was wrapped tightly around the imported Swiss cheese, so that there was no intervening air space. The cream cheese was also wrapped with tin foil, but the wrapping was not nearly so tight and apparently afforded little protection.

EFFECT OF BOILING ON HYDROCYANIC ACID IN FUMIGATED FOOD PRODUCTS

To determine what effect cooking would have on the hydrocyanic acid content of fumigated foods, some foodstuffs were fumigated in the usual way and the hydrocyanic acid was determined, after which the products were boiled with water in open flasks. At the end of 10 minutes and 30 minutes flasks were removed from over the burner and the hydrocyanic acid content was determined. The results are given in Table 5.

TABLE 5.—*Effect of boiling with water on hydrocyanic acid content of fumigated food products*

Product	Hydrocyanic acid present (parts per million)		
	Original condition	After being boiled for—	
		10 minutes	30 minutes
Apples, dried	170	3	0
Prunes	55	11	6
Cereal, ground wheat	220	55	33
Ham, sliced	170	8	6
Hamburger steak	83	4	2

In the absence of added acid, boiling for 10 minutes was not sufficient to remove all the hydrocyanic acid in any product. Boiling for 30 minutes removed all of it only from dried apples, and this may be explained by the presence of acid in the apples. The unusually large quantity of hydrocyanic acid found in the ground-wheat cereal was probably retained because the material was so thick that it had to be boiled slowly to prevent foaming.

SUMMARY

Dried fruits were fumigated with hydrocyanic acid gas. The fumigant remaining was determined on the day of fumigation and at intervals of 1, 7, 30, and 90 days thereafter.

All fruits which were not in tight packages absorbed some hydrocyanic acid. This was gradually dissipated, although a small quantity was left in many of the fruits at the end of 90 days.

Dried fruits fumigated in commercial packages did not absorb as much hydrocyanic acid as those fumigated without such protection. No fumigant was absorbed by apricots tightly packed in a box lined with waxed paper, and the gas did not penetrate to the center of the box of tightly packed figs. This indicates that the process of fumigation used would not be effective as a method of freeing dried fruits from insects if the fruits are tightly packed and wrapped in waxed paper.

Candies absorbed a comparatively small quantity of hydrocyanic acid. The original absorption of nut meats was high, but most of the fumigant was dissipated in a very short time. Cocoa absorbed a high proportion of the fumigant and retained it for some time.

No hydrocyanic acid was absorbed through the rind of an American Swiss cheese. No fumigant penetrated to cheese tightly wrapped in tin foil, but the absorption was as high in cheese loosely wrapped in tin foil as in that which was not wrapped.

Boiling with water in the absence of added acid for 30 minutes was not always sufficient to entirely remove the hydrocyanic acid.

No conclusions as to the safety of fumigated foods for human consumption are drawn from the results reported in this bulletin. Chemical observations alone are reported here. Determinations of the quantities of hydrocyanic acid injurious to health lie in the domain of the pharmacologist.

LITERATURE CITED

(1) Anonymous.
Ship fumigation. Preliminary report of the board appointed by the Surgeon General to investigate the subject of fumigation of ships. *In* U. S. Treasury Dept., Public Health Rpts. (1922), *37:* 2744–7.

(2) Bonjean, Ed.
Emploi de l'acide cyanhydrique (prussique) pour la destruction des rats, des parasites et des insectes. *In* Rev. hyg. (1922), *44:* 776–794.

(3) DeOng, E. R., and Roadhouse, C. L.
Cheese pests and their control. Calif. Agr. Expt. Sta. Bul. 343 (1922), p. 419–424.

(4) Heerdt, W.
Zyklon-Verfahren. *In* Praktische Desinfektor (1921), *13:* 9–11.

(5) Jansen, J. D., Schut, W., and Wagenaar, M.
Eenige Mededeelingen over de adsorptie van cyclon door vershillende levensmiddelen. *In* Chem. Weekblad. (1922), *19:* 373–375.

(6) Lutrario.
Expériences sur la diffusion de l'acide cyanhydrique dans les locaux fermés, et sur l'action de cet acide sur certaines marchandises (substances alimentaires et tissus) et sur quelques animaux parasites. *In* Bull. off. intern. hyg. pub. (1921), *13:* 367–376.

(7) Simmons, P.
Hydrocyanic acid retained by fumigated cheese. *In* J. Econ. Entomol. (1924), *17:* 416–17.

(8) Stock, P. G., and Monier-Williams, G. W.
Preliminary report on the use of hydrogen cyanide for fumigation purposes. Great Britain Ministry of Health, Rpt. Pub. Health Med. Subjects 19 (1923), p. 19.